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Kling, Jens; Vestergaard, Jacob Schack; Dahl, Anders Bjorholm; Stenger, Nicolas; Booth, Tim ; Bøggild, Peter; Larsen, Rasmus; Wagner, Jakob Birkedal; Hansen, Thomas Willum

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1 **Pattern recognition approach to quantify the atomic structure of graphene**

2 Jens Kling^{*,1,5}, Jacob S. Vestergaard², Anders B. Dahl², Nicolas Stenger^{3,5}, Tim J. Booth⁴, Peter
3 Bøggild^{4,5}, Rasmus Larsen², Jakob B. Wagner¹, Thomas W. Hansen^{1,5}

4 ¹ *Center for Electron Nanoscopy (DTU Cen), Technical University of Denmark, Fysikvej 307, 2800*
5 *Kgs. Lyngby, Denmark*

6 ² *Department of Applied Mathematics and Computer Science (DTU Compute), Technical University*
7 *of Denmark, Matematiktorvet 303B, 2800 Kgs. Lyngby, Denmark*

8 ³ *Department of Photonics Engineering (DTU Fotonik), Technical University of Denmark, Ørstedes*
9 *Plads 343, 2800 Kgs. Lyngby, Denmark*

10 ⁴ *Department of Micro- and Nanotechnology (DTU Nanotech), Technical University of Denmark,*
11 *Ørstedes Plads 345E, 2800 Kgs. Lyngby, Denmark*

12 ⁵ *Center for Nanostructured Graphene (CNG), Technical University of Denmark, Ørstedes Plads*
13 *345E, 2800 Kgs. Lyngby, Denmark*

14

15 We report a pattern recognition approach to detect the atomic structure on high-resolution
16 transmission electron microscopy images of graphene. The approach provides quantitative
17 information such as carbon-carbon bond lengths and bond length variations on a global and local
18 scale alike.

19 -----

20 Graphene is considered a key material for future electronic applications with the possibility of very
21 high performance transistors [1], spintronics [2] and ballistic devices even at room temperature [3].
22 The degree to which the actual performance of graphene devices can live up to the theoretical
23 predictions depends critically on the presence of defects, atomic configuration of edges. In essence,
24 any deviations from perfect lattice periodicity can be important, which for instance is manifested in
25 the sensitivity of electronic properties to strain [4].

* Corresponding author. E-mail: jenk@cen.dtu.dk (J. Kling), Phone: +4545256487

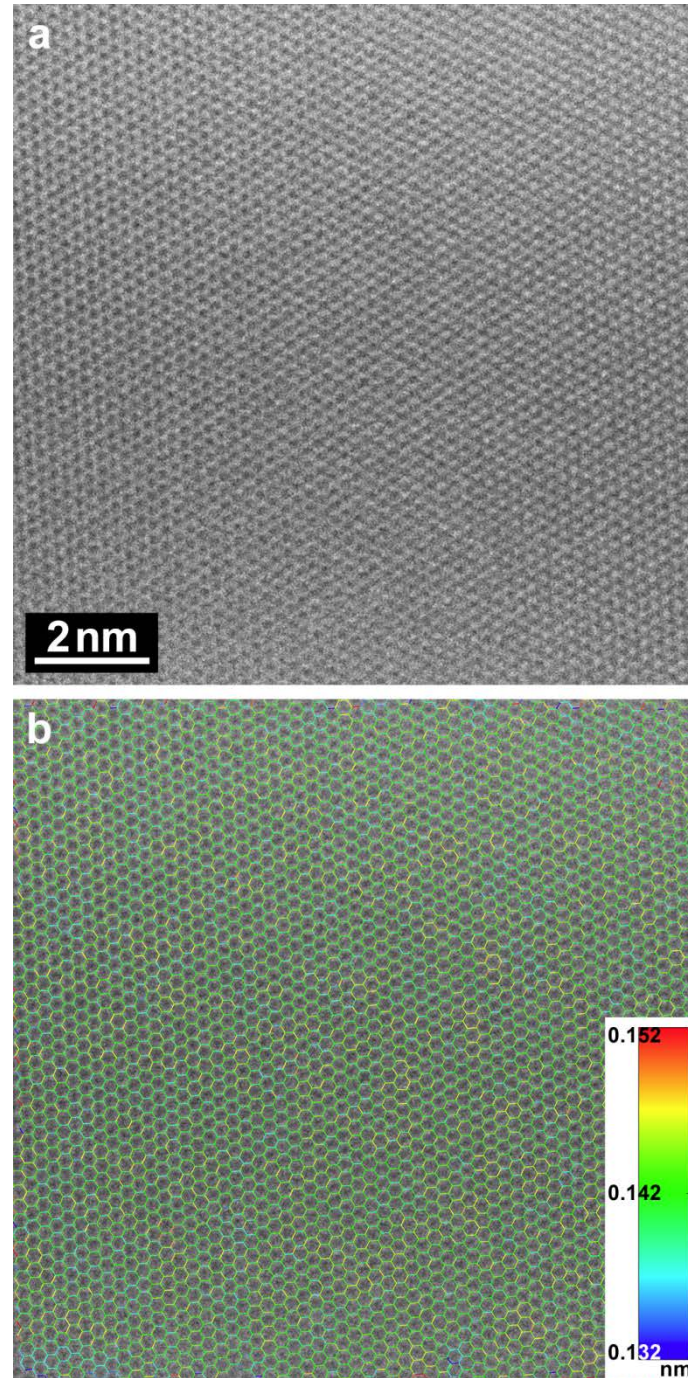
1 Transmission electron microscopy (TEM) in general and high-resolution TEM (HRTEM) in
2 particular can provide information about the atomic structure and defect landscape of graphene [5].
3 While important parameters like the carbon-carbon (C-C) bond length are possible to determine,
4 this is usually done manually in small areas [6], due to time-consuming work of manually analyzing
5 the HRTEM images. Here we describe a method for fast, automatic structure detection in graphene
6 in a large number of sequentially acquired HRTEM images. The method enables quantitative
7 information such as C-C bond length or bond length variations to be determined from images in a
8 fast and reliable way, and can be used on many images to allow access to this information from a
9 large area.

10 Suspended single-layer graphene synthesized by chemical vapor deposition (CVD) (Graphenea,
11 Spain) or by mechanical exfoliation of graphite [7] and transferred to TEM grids have been
12 investigated using the automatic method. The graphene is imaged using a FEI Titan 80-300
13 Environmental TEM (ETEM) equipped with a monochromator at the electron gun and a spherical
14 aberration (Cs)-corrector for the objective lens. All images are acquired with the microscope
15 operated at 80 kV, which is below the knock-on threshold of carbon atoms in pristine graphene [8].

16 In order to optimize the imaging conditions and thereby the input for the structure detection, the
17 electron beam energy spread was reduced to below 0.3 eV using the monochromator, while the Cs
18 corrector was aligned to minimize the spherical aberration Cs. These conditions result in a
19 resolution better than 0.12 nm, allowing us to resolve the 110-reflections of graphene and visualize
20 the atomic structure accurately. The images are recorded using a Gatan US1000 CCD camera with
21 an exposure time of 1 s.

22 The structure determination algorithm involves several steps. Utilizing Fourier transformation and
23 local maxima detection, the mean graphene structure over the whole image is detected and used as
24 starting point. The basis is a triangular lattice (triangulation) with a side length of roughly 0.247 nm,
25 connecting three hexagonal centers (nodes) of the graphene structure. Hexagon center positions in
26 the image are recognized as contrast extremes, minima for negative Cs or maxima for positive Cs.
27 Nodes and triangles are removed from the triangulation when the local contrast properties or

1 geometry deviate significantly from the expectations, and consequently areas like holes or
2 amorphous material can be automatically omitted. In a final step, the node positions are adjusted by
3 grid matching [9]. These steps enable a full reconstruction of the atomic structure of the observed
4 graphene area in most cases. A more detailed description of the algorithm will be published
5 elsewhere.



6
7 **Figure 1:** Pristine graphene. (a) HRTEM image, (b) image overlaid with the detected and
8 reconstructed graphene structure. The color coding represents the C-C bond lengths. A homogenous
9 distribution of bond lengths is observed.

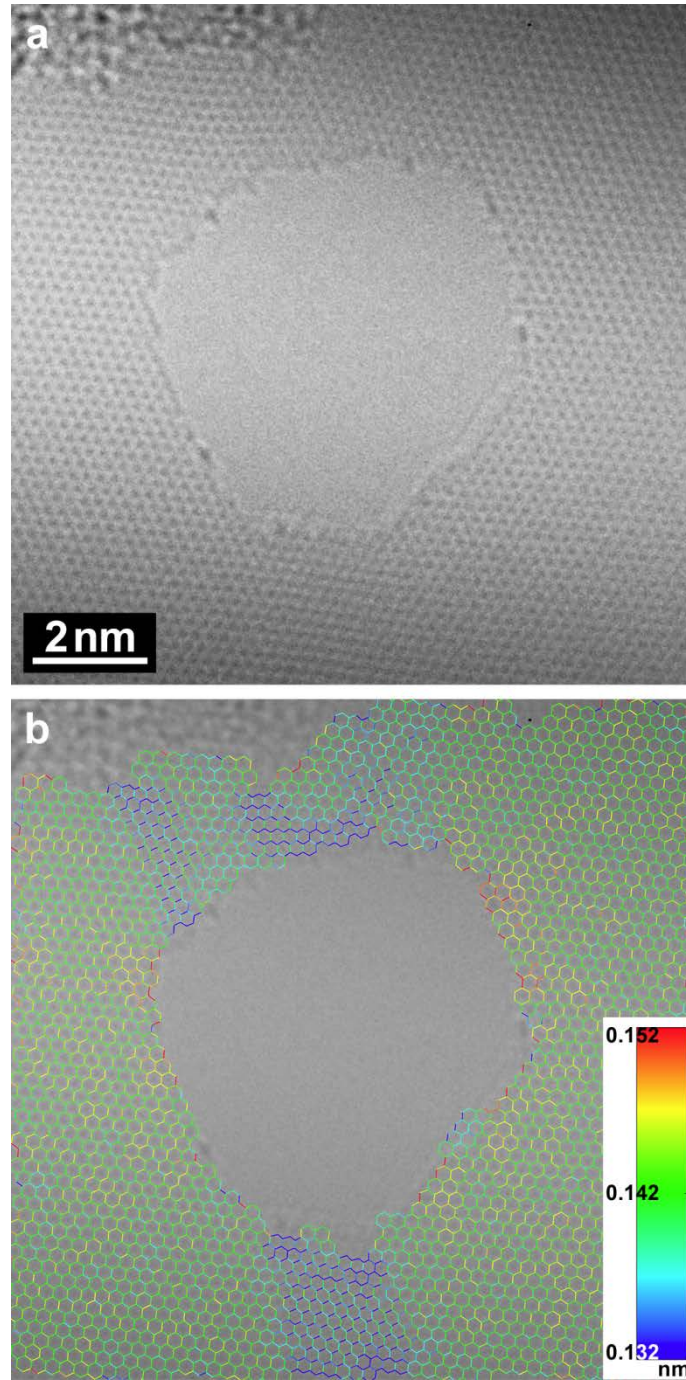
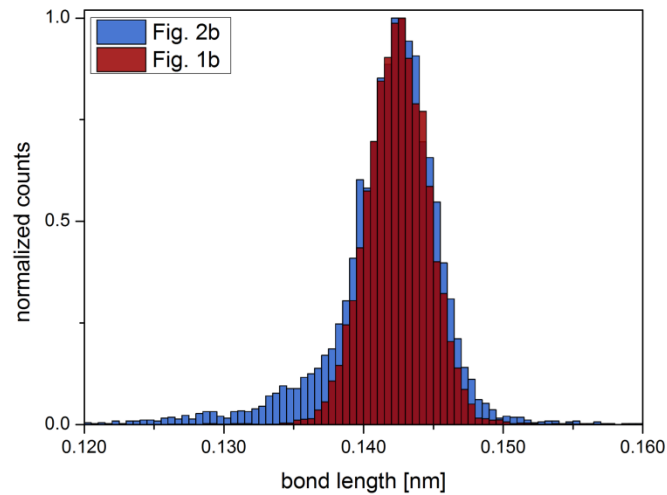


Figure 2: Graphene with a hole, formed under the influence of the electron beam. (a) HRTEM image, (b) image overlaid with the detected and reconstructed graphene structure. Color coding is the same as in Fig. 1b. Significantly shorter bond lengths with preferred orientation are observed above and below the hole.

Figures 1a and 2a show HRTEM images of two different areas of graphene. The hexagonal honeycomb lattice is easily recognized. Using negative Cs imaging, the carbon atoms are bright spots, with the centers of the hexagons appearing dark. In Fig. 1a, a hole in the graphene, formed

1 under the influence of the electron beam is observed. Due to the inherent small signal-to-noise
2 (S/N) ratio in the graphene image [5], as well as the continuous beam induced changes of the atomic
3 structure at the edge [10], the termination of the hole cannot be completely resolved. Nevertheless, a
4 predominant zigzag termination is assumed, which is in agreement with previous findings [11]. In
5 Fig. 1b and 2b, the reconstructed graphene structure determined from the algorithm is overlaid,
6 showing the actual hexagonal lattice of the graphene. The color coding represents the C-C bond
7 lengths. As the absolute value retrieved from the images is dependent on the imaging conditions and
8 the calibration, only the relative change within an image is considered. Figure 1b, representing a
9 pristine area, gives the impression of a homogenous distribution of bond lengths. This is reflected in
10 the bond length histogram (Fig. 3 red) which exhibits a normal distribution.



11
12 **Figure 2:** Histograms of the detected bond lengths from Fig. 1b (red) and Fig. 2b (blue). The bond
13 lengths are binned by 0.5×10^{-3} nm steps; the counts are normalized for simpler shape comparison
14 between the two histograms. The red histogram shows a normal distribution. The blue histogram
15 exhibit a tail towards shorter bond length.

16
17 For the case of a defective structure, as in Fig. 2, the algorithm detects nearly all graphene
18 hexagons. The only exceptions are structures close to the hole and the edge termination itself, which
19 most likely is due to insufficient imaging conditions, as mentioned above. The area of amorphous
20 carbon from the transfer process or synthesis (top left) was disregarded manually, but the area of the

1 hole is detected by the algorithm and automatically left out in the analysis. A homogenous
2 distribution of bond lengths is observed to the left and right of the hole. For the areas above and
3 below the hole, significantly shorter bond lengths are detected. This is obvious in the histogram as
4 well (Fig. 3 blue), where a tail towards shorter bond length is visible. Suspended graphene is known
5 to form out-of-plane ripples [12], which are expected to have a lateral size of 2 – 20 nm and a
6 height of 0.2 – 1 nm, with an inclination of $\approx 5^\circ$ from the horizontal flat sheet. In this case, the
7 projection of the bond length is measured from the image, making the lengths appear shorter. The
8 shortest observed bond lengths above and below the hole have a preferred orientation, almost
9 horizontal in this image. This may be explained by the graphene sheet being slightly folded, as this
10 should lead to a change in z-height as well as elastic deformation and strain mainly in the direction
11 perpendicular to the fold, as we observe in the image. For an almost flat sheet, these bond lengths
12 would represent a strain of about 7 – 8 %; a pure inclination without bond length change would give
13 an angle of about 22° between the two adjacent carbon atoms and an offset in height of about 0.05
14 nm. The rearrangement and knock-out of carbon atoms under the electron beam at the edge of the
15 hole [10] can lead to structural deformation as well. A combination of both, a real shorting of the
16 bond length and an artificial shortening due to projection in the image, is the most realistic
17 explanation of our finding. It is important to notice, that even though the shorter bond lengths are
18 represented in the global histogram, the local information, where these bonds actually appear in the
19 structure, is only available in the image itself. The acquired local information in the bond length
20 indicates a possible correlation between measured short bond lengths and folding of graphene. The
21 nature of the bond length shortening will be clarified in a future study.

22 The automated structure detection for quantitative information extraction from high-resolution TEM
23 images is possible for a large amount of images at relatively low time-cost and minimum manual
24 interaction, making it easier and more feasible to follow structural changes in a series of images.
25 Incremental and time dependent structural changes caused by either electron beam induced effects
26 and/or external stimuli like temperature, current etc. can be monitored and quantified in future
27 investigations in greater depths than standard image analysis procedures allow.

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